U.S. DEPARTMENT OF COMMERCE
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PB-258 361

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GCA Corp, Bedford, Mass GCA Technology Div

Prepared for

Environmental Protection Agency, Research Triangle Park, N C

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VOLUME I
FINAL REPORT

[redacted]

Prepared for
[redacted]

January 1976

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
Assessment of Methyl Methacrylate as a Potential Air Pollution Problem

5. REPORT DATE
January 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Robert M. Patterson
Eric Garshick
Mark I. Bornstein

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
GCA Corporation
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-1337

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

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Volume III	Ethylene Dichloride	Volume X	Ortho-Xylene
Volume IV	Benzene	Volume XI	Maleic Anhydride
Volume V	Acetone	Volume XII	Dimethyl Terephthalate
Volume VI	Acrylonitrile	Volume XIII	Adipic Acid
Volume VII	Cyclohexanone	Volume XIV	Phthalic Anhydride

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Methyl Methacrylate Ambient Concentrations Measurement Methods Emission Sources Emission Controls Industrial Chemicals Physical Properties Health Effects Chemical Properties Welfare Effects	Methyl Methacrylate Air Pollution Assessment Air Pollution Control Organic Chemicals	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	28
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	4.00

EPA Form 2220-1 (9-73)

PRICES SUBJECT TO CHANGE

GCA-TR-75-32-G(9)

ASSESSMENT OF METHYL METHACRYLATE AS A POTENTIAL AIR POLLUTION PROBLEM

Volume IX

by

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Bedford, Massachusetts

January 1976

Contract No. 68-02-1337
Task Order No. 8

EPA Project Officer

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park
North Carolina 27711

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This report was furnished to the U.S. Environmental Protection Agency by the GCA Corporation, GCA/Technology Division, Bedford, Massachusetts 01730, in fulfillment of Contract No. 68-02-1337, Task Order No. 8. The opinions, findings, and conclusions expressed are those of the authors and not necessarily those of the U.S. Environmental Protection Agency or of the cooperating agencies. Mention of company or product names is not to be considered as an endorsement by the U.S. Environmental Protection Agency.

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Volume XII	Dimethyl Terephthalate
Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Methyl methacrylate is a colorless, flammable liquid with an acrid, fruity odor. The primary method of manufacture is based on the reaction of acetone and hydrogen cyanide, and the primary use is in the production of resins or plastics such as Plexiglass and Lucite.

Methyl methacrylate vapor is an acute irritant, with eye and mucous membrane irritation occurring at concentrations of 125 ppm. At higher concentrations death will ultimately result from pulmonary edema, although such high concentrations cannot be tolerated voluntarily by man. It can be detected in air by smell at concentrations of less than 1 ppm. However, the U.S. occupational standard for an 8-hour time weighted average is 100 ppm, based on measurable acute human sensory response. In the bloodstream, methyl methacrylate has been linked to cardiac arrest and other cardiovascular effects caused by its hypotensive (promoting low blood pressure) properties. No lasting chronic effects have been recorded.

Simple diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at less than 2 ppm. The maximum 24-hour average ambient concentration might be expected to be less than 1 ppm.

About 766 million pounds of methyl methacrylate were produced at seven plants in 1974, with 45 percent of this being used in the manufacture of acrylic sheets, and 23 percent used in the surface coating industry. Production is expected to increase by 10 percent per year for the next several years. The primary emission sources in descending order are

production, end product manufacture, and bulk storage. Total emissions are estimated to have been about 7.9 million pounds in 1974.

Although emission controls specifically for methyl methacrylate are not reported, two types of controls are used extensively by the chemical industry to control hydrocarbon emissions. These are vapor recovery and incineration. Control by adsorption on activated charcoal is used when recovery is economically desirable. The primary advantage of incineration is that low concentrations may be oxidized with only small supplemental fuel requirements. Fixed roof storage tanks can be controlled by venting to an adsorber or to an incinerator, or they can be converted to floating roof design.

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, it appears that methyl methacrylate as an air pollutant does not pose a threat to the health of the general population. In addition, methyl methacrylate does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Methyl methacrylate is a colorless, flammable liquid with an acrid, fruity odor. The primary method of manufacture is based on the reaction of acetone and hydrogen cyanide, with subsequent esterification to the methyl ester using methanol. Most methyl methacrylate is polymerized into resins or plastics such as Plexiglass (Rohm and Haas) or Lucite (DuPont). Such materials are widely used in paints, protective coatings, lubricants, floor polishes, and textiles. Significant physical and chemical properties are listed in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF METHYL METHACRYLATE

Synonyms	methacrylic acid, methyl ester
Chemical formula	$CH_2 = C(CH_3)\ COOCH_3$
Molecular weight	100.1
Boiling point	101.0°C
Melting point	-50°C
Specific gravity	0.936 at 20°C
Vapor density	3.60 (air = 1) at boiling point of methyl methacrylate
Vapor pressure	35 mm Hg at 20°C
Solubility	Slightly soluble in water
Explosive limits	1.7 to 8.2% by volume in air
Ignition temperature	421°C
Flash point	29.5°C (closed cup)
At 25°C and 760 mm Hg	1 ppm = 4.08 mg/m^3
	1 mg/m^3 = 0.25 ppm

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Methyl methacrylate vapor is an acute irritant. Inhalation at concentrations as low as 125 ppm has caused eye and mucous membrane irritation.[1] Other symptoms may include irritability, increased salivation, headache, drowsiness, and nausea.[2] At higher levels there will be an increase in drowsiness, skin irritation, hypotension (low blood pressure), and marked respiratory tract irritation leading to unconsciousness. Death will follow due to pulmonary edema and other lung damage. In animals death has resulted as a result of exposure above 10,000 ppm for 3 hours (See Table 2). However, the vapors carry very strong warning properties, and it is unlikely that such high levels could be tolerated voluntarily by man. It can be detected in air by smell without any background interferences at 0.21 ppm.[3] Headache, nausea and other symptoms of exposure to tolerable levels disappear after removal of the vapor.

The toxicity of methyl methacrylate once in the bloodstream has been shown in studies concerning the hazards of methyl methacrylate bone cement used during joint replacement. The use of the cement in man has been linked to a high incidence of cardiac arrest and other cardiovascular side effects caused by its hypotensive properties.[4] Joint replacement operations are usually performed on older patients, usually with a history of heart trouble. Human methyl methacrylate blood levels after surgery have ranged between 1 and 200 mg/100 ml. Human reaction to such levels has included operative and postoperative pulmonary hypoxia,[5] or a deficiency of oxygen in the lung tissue.

Chronic Poisoning - The U.S. occupational standard for an 8-hour time weighted average is 100 ppm, based on acute human sensory response. Injury from chronic exposure to low levels of methyl methacrylate vapor has not been documented in man. One report of chronic exposure involves dental students fabricating dentures and refers to the characteristic acrid odor permeating an entire work area.[6] The principal toxic effect exerted by the vapor was nausea and loss of appetite both during and after exposure. There were no lasting toxic effects.

Effects on Animals

Acute animal response to high concentrations of methyl methacrylate vapors is presented in Table 2.[7,8] Animal response to single 8-hour exposures is presented in Table 3.[8,9,10] Inhalation produced an increased rate of respiration, lachrymation, mucous membrane irritation, excess salivation and vomiting. Respiration then slowed, reflex activity was lost, and the animals died in a coma. The heart, adrenals, spleen, and gastrointestinal tract of the animals showed no damage. The blood picture was normal. Lungs, trachea, and bronchi were markedly congested, edematous, and spotted with small areas of hemorrhage. Liver and kidney degeneration was also found in some animals.

Doses of 10 cc/kg body weight applied to the clipped abdomen of rabbits produced temporary local irritation, with the animals recovering within an hour.[10] Three drops of liquid methyl methacrylate dropped into the eyes of rabbits produced irritation and edema. In 24 to 72 hours, the eyes returned to normal.[8] The acute oral LD_{50} for rats is 8.4 g/kg body weight, and for rabbits it is 6.7 g/kg body weight.[9] Ingestion produces the same symptoms of poisoning as inhalation.

Rabbits injected intravenously with 0.03 to 0.04 cc/kg body weight showed a sudden fall in arterial pressure, followed by recovery in 3 to 4 minutes. The respiration became stimulated and remained elevated for 20 to 30

Table 2. ACUTE ANIMAL RESPONSE TO METHYL METHACRYLATE VAPOR INHALATION[7,8]

Animal	Number used	Dose, ppm	Duration, hrs	Response
Mice	15	15,140	3	All died (1 - 3 hr.)
Guinea pigs	6	16,265	4 1/4	All died (2 3/4 - 4 1/4 hr.)
Dogs	2	10,000	3	Both died (2 - 3 hr.)
Dogs	2	16,265	1 1/2	Both died (1 - 1 1/2 hr.)
Rabbits	NA[a]	13,500	3	Death

[a]Not available.

Table 3. RESPONSE TO SINGLE 8-HOUR EXPOSURE TO METHYL METHACRYLATE[8,9,10]

Animal	Number used	Dose, ppm	Response	Reference
Rabbits	NA[a]	3,500	Survived	10
Guinea pigs	NA	3,500	Survived	10
Rats	NA	3,500	Survived	10
Rabbits	NA	4,650	Died in 1 1/2 hrs.	10
Guinea pigs	NA	4,650	Died in 5 hrs.	10
Rabbits	NA	4,650	Died in 2 1/2 hrs.	10
Rabbits	NA	3,750	Approximate LD_{50}	9
Mice	20	6,120	1 died in 3 hrs.	8
Mice	15	11,690	2 died in 3 hrs, 9 died in 5 hrs.	8
Mice	15	15,140	All died in 3 hrs.	8
Mice	20	23,620	All died in 2 1/4 hrs.	8

[a]Not available.

minutes. However, the respiration then decreased with each dose until the animal died. In two separate investigations[8,10] the heart was seen to continue beating after respiratory stoppage, implicating respiratory damage as the cause of death. Pulmonary lesions have been found in dogs with blood methyl methacrylate levels as low as 5 mg/100 ml, and death has occurred where levels were 125 mg/100 ml following intravenous administration.

Chronic Poisoning - Animal response to chronic exposure to methyl methacrylate vapor is presented in Table 4.[8] No deaths were seen until values above 10,000 ppm were reached. Death was due to chronically induced pulmonary damage leading to respiratory failure.

Table 4. ANIMAL RESPONSE TO CHRONIC METHYL METHACRYLATE INHALATION

Animal	Number used	Dose, ppm	Duration		Response
			hrs/day	days	
Mice	20	10,000	1/2	15	1 died (5th day)
Mice	20	10,000	1 1/2	15	2 died (2nd-3rd days)
Guinea pigs	6	9,630	3	15	All lived
Guinea pigs	6	16,050	3	3	All died (1-3 days)
Dogs	2	10,000	1/2	15	Both lived
Dogs	2	11,500	1/2	15	1 died (14th day)
Dogs	2	11,500	1 1/2	8	Both died (6-8 days)

Effects on Plants

The effects of methyl methacrylate on vegetation have not been documented in the literature.

Effects on Materials

Methyl methacrylate vapors are uninhibited and may polymerize in vents and storage containers. Heat may cause polymerization. Contact with nitrates, oxidizing materials (peroxides), and strong alkalies may cause fire and explosion as a result of chemical reaction.[7]

AMBIENT CONCENTRATIONS AND MEASUREMENTS

Ambient Concentration Estimates

The largest installation for methyl methacrylate production is located in a town of about 13,000 population, and it has a capacity of about 550 million lb/yr. Assuming a 0.5 percent loss, this converts to an emission rate of:

$$\frac{(0.005 \text{ emission factor})\ (550 \times 10^6 \text{ lb/yr})\ (453.6 \text{ g/lb})}{3.1536 \times 10^7 \text{ sec/yr}}$$

$$= 39.6 \text{ g/sec of methyl methacrylate.}$$

Some assumptions must be made regarding this chemical release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant where methyl methacrylate vapor leaks to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility.[11] To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100m/4.3 = 23.3m \ .$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or

$$= \frac{39.6}{(2)\pi(36)\ (18.5)} e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 8.18 \times 10^{-3} \ g/m^3$$

for a 10-minute average concentration. Over a period of an hour this becomes 8.18×10^{-3} (0.72) = 5.89×10^{-3} g/m^3 or 1.5 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 0.8 ppm.

Methyl Methacrylate Measurement Techniques

Two analytical methods are available for the determination of methyl methacrylate. Both methods use potassium permanganate; however, the procedures do vary in the types of reagents used for analysis.

The first method[12] will allow the determination of methyl methacrylate in air to concentrations as low as 10 ppm. The air sample is collected in a midget impinger containing potassium permanganate, sodium hydroxide and telluric acid. Approximately a 200 ml air sample is bubbled through

the impinger until the permanganate changes color from pink to bluish-green. The concentration is then determined from a calibration curve showing air volume versus parts per million.

Interferences may result from compounds containing double-bonded carbon atoms. This method may not be suitable for air pollution work but is satisfactory for industrial hygiene field work. The procedure requires about 30 minutes for completion of the test.

The second method[13] is similar in procedure to the first method; however, the reagents used are potassium permanganate, sulfuric acid and potassium oxalate. The solution is allowed to stand in the dark prior to the addition of the oxalate. After this waiting period, excess sulfuric acid is added, then the sample is titrated with potassium permanganate. The results of the titration are compared against a calibration curve. Concentrations as low as 3 ppm have been detected by this method. Interferences are present from the same compounds mentioned for the first method.

Although neither method is sensitive enough to determine expected ambient concentrations, either method could be used for field sampling if concentrations above 3 or 10 ppm were suspected.

SOURCES OF METHYL METHACRYLATE EMISSIONS

Methyl Methacrylate Production and Consumption

The production of methyl methacrylate in 1974 was approximately 766 million pounds,[14] and it is expected to increase at 10 percent per year for the next several years. The largest end use of methyl methacrylate is for the production of acrylic sheet, accounting for approximately 45 percent of total production. Acrylic sheets are used primarily for advertising signs, lighting fixtures, and as a replacement for glass windows. The surface coating industry is the next major user of methyl methacrylate, consuming an estimated 23 percent of the total production, with latex paints, acrylic lacquer resins, and acrylic enamels being the

primary markets. The consumption of methyl methacrylate for all end products is shown in Table 5.[15] This table also shows the expected growth rates for each sector of the market.

Table 5. ESTIMATED METHYL METHACRYLATE CONSUMPTION - 1974[15]

	Million pounds	Expected annual growth rate
Acrylic sheet	344,850	11%
Surface coating resins	176,256	9%
Molding and extrusion powders	160,929	9%
Emulsion polymers	51,874	7%
Acrylic fibers	12,968	7%
Polyester modification	6,484	7%
Other	12,969	7%
Total	766,330	10%

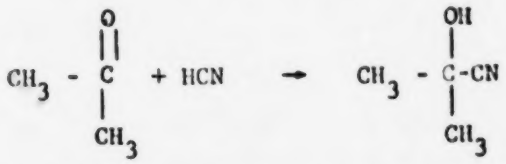
Methyl Methacrylate Sources and Emission Estimates

Primary sources of emissions of methyl methacrylate occur from methyl methacrylate production, end product manufacture, and bulk storage. Total emissions of methyl methacrylate are estimated to be 7.9 million pounds, representing 1.0 percent of total production as shown in Table 6.

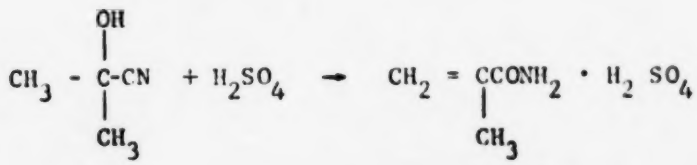
Table 6. SOURCES AND EMISSION ESTIMATES OF METHYL METHACRYLATE - 1974

Source	Emissions, million pounds
Methyl methacrylate production	3.8
End product manufacture	3.8
Bulk storage	0.3
Total	7.9

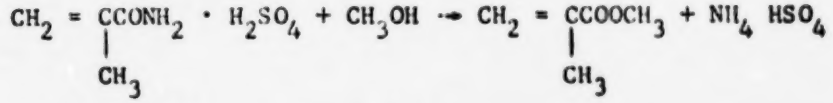
All methyl methacrylate produced in the United States is based on the acetone cyanohydrin process. During this process, acetone and hydrogen cyanide are reacted to form methacrylamide sulfate. The intermediate, methacrylamide sulfate, is not isolated but is reacted directly with methyl alcohol to form a crude methyl methacrylate and ammonium bisulfate. This crude product is then distilled to give a pure methyl methacrylate. The reactions for this process are given below.



acetone — hydrogen cyanide — acetone cyanohydrin



acetone cyanohydrin — sulfuric acid — methacrylamide sulfate



methacrylamide sulfate — methyl alcohol — methyl methacrylate — ammonium bisulfate

Of the seven production sites in the U.S., only four plants produce a crude methyl methacrylate product. The remaining three plants only distill the crude monomer which is produced at a central production site. Appendix A lists producers and locations.

Since data do not exist in the literature concerning emissions from the manufacture of methyl methacrylate, it is estimated that 0.5 percent of total production is lost from manufacturing operations. This factor is based upon data available in AP-42[16] and emissions data for other similar processes. The major sources of emissions are primarily from vents, condensers, valves, and reactors. Using the emission factor of 0.5 percent and the estimated 1974 production rate of 766.33 million pounds results in 3.83 million pounds of methyl methacrylate lost to the atmosphere.

Similarly, it is estimated that emissions from the use of methyl methacrylate to manufacture other products is also 0.5 percent. Since the total production is used for the manufacture of end products, emissions from this source are also 3.83 million pounds.

The last major source of emissions is from bulk storage. Using the emission factors presented in AP-42[16] and assuming that all storage tanks are fixed roof, emissions are 0.3 million pounds.

METHYL METHACRYLATE EMISSION CONTROL METHODS

The literature does not report specific control equipment for methyl methacrylate emissions, but it does report on control devices for other similar hydrocarbons. Two types of control devices are presently used by the industry to control hydrocarbon emissions: vapor recovery and incineration. Both systems have reported efficiencies of at least 95 percent.

Control of hydrocarbon emissions by adsorption on activated charcoal is generally applied when recovery of adsorbed material is economically desirable. Adsorption should be used when concentrations of hydrocarbons are greater than 2500 ppm.[17] Other applications are for the control of very low concentration hydrocarbons that are poisonous to

catalytic incinerators, and for collection and concentration of low concentration emissions for subsequent disposal by incineration. Cost data for the cases utilizing adsorption are presented in Tables 7 and 8. The three cases presented are adsorption with solvent recovery, adsorption with incineration, and adsorption with incineration plus heat recovery.

Table 7. ESTIMATED INSTALLED COSTS[a] OF ADSORPTION SYSTEMS[18]

Adsorber capacity, SCFM - based on 25% lower explosive limit	1,000	10,000	20,000
With solvent recovery, $	74,000	162,300	280,000
With thermal incinerator/no heat recovery, $	89,500	202,000	344,000
With thermal incineration/ primary heat recovery, $	101,500	255,000	431,000

[a]Cost data updated to 1st quarter 1975.

Table 8. ESTIMATED ANNUAL OPERATING COSTS[a] OF ADSORPTION SYSTEMS[18]

Adsorber capacity, SCFM - based on 25% lower explosive limit	1,000	10,000	20,000
With solvent recovery, $/yr	13,200	10,479[b]	37,200[b]
With thermal incineration/no heat recovery, $/yr	23,400	64,300	123,200
With thermal incineration/ primary heat recovery, $/yr	25,600	82,000	141,600

[a]Cost data updated to 1st quarter 1975.

[b]Indicates a savings.

Control of methyl methacrylate emissions by incineration or catalytic oxidation involves direct oxidation of the combustible portion of the effluent, the desired ultimate products being water and carbon dioxide.

The primary advantage of catalytic incineration is that extremely small concentrations of organics can be oxidized with only small amounts of supplemental fuel required. The main disadvantages are the higher capital cost and the fact that certain hydrocarbons may poison the catalyst. Cost data for thermal and catalytic incinerators with and without heat recovery are presented in Tables 9 and 10.[18]

Table 9. ESTIMATED INSTALLED COSTS[a] OF THERMAL AND CATALYTIC INCINERATORS[18]

Incinerator capacity, SCFM-based on 25% lower explosive limit	1,000	10,000	20,000
Installed costs, $			
Catalytic without heat recovery	43,500	272,000	504,600
Catalytic with primary heat recovery	54,100	306,000	573,900
Catalytic with primary and secondary heat recovery	68,300	361,800	666,400
Thermal without heat recovery	27,200	92,500	137,400
Thermal with primary heat recovery	40,300	144,200	232,600
Thermal with primary and secondary heat recovery	54,400	200,000	322,300

[a]Cost data updated to 1st quarter 1975.

Table 10. ESTIMATED ANNUAL OPERATING COSTS[a] OF THERMAL AND CATALYTIC INCINERATORS[18]

Incinerator capacity, SCFM - based on 25% lower explosive limit	1,000	10,000	20,000
Operating costs, $/yr			
Catalytic without heat recovery	16,200	102,800	195,000
Catalytic with primary heat recovery	16,400	78,500	177,900
Catalytic with primary and secondary heat recovery	19,300	108,700	203,700
Thermal without heat recovery	12,000	54,300	96,700
Thermal with primary heat recovery	11,500	36,300	59,200
Thermal with primary and secondary heat recovery	14,400	50,800	84,500

[a]Cost data updated to 1st quarter 1975.

Control of emissions from storage tanks will require the use of floating roof tanks or venting the emissions to the previously mentioned adsorber or incinerator. Emissions from fixed roof tanks can be vented to either system without any major increase in cost. If these systems are not available, fixed roof tanks should be switched to floating roof tanks resulting in a 70 percent reduction of emissions. Figure 1 provides estimated costs of various gasoline storage tanks.[18] These equipment cost estimates can also be applied to methyl methacrylate. As can be seen, conversion of fixed roof to floating roof tanks by installation of internal floating covers is more economical than the installation of new pontoon floating tanks.

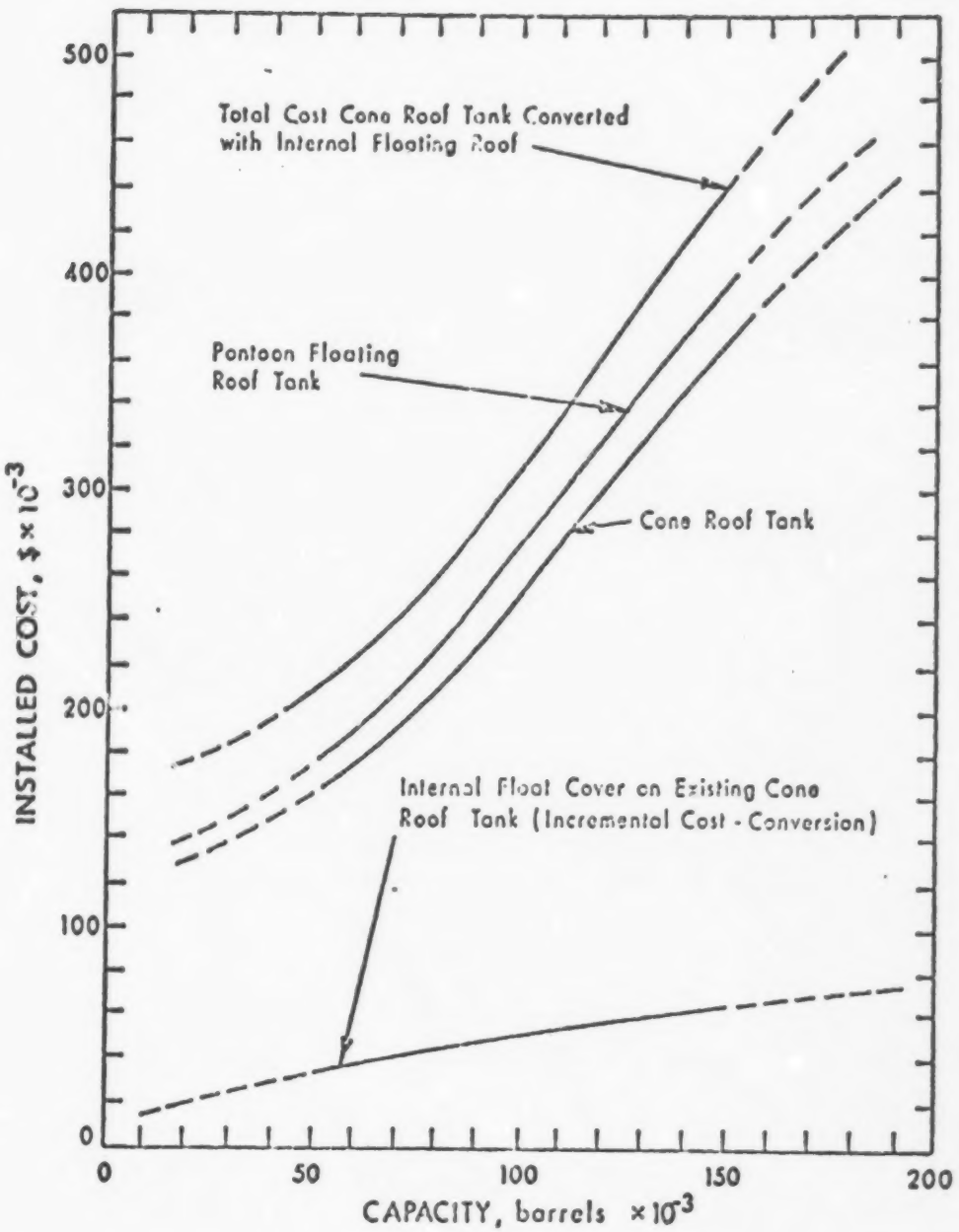


Figure 1. Estimated installed cost of methyl methacrylate storage tanks (equipment costs assumed to be the same as gasoline storage tanks)[18]

SECTION III

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APPENDIX A

METHYL METHACRYLATE MANUFACTURERS

		Annual capacity,* million pounds
American Cyanamid Co.	Fortier, Louisiana	80
DuPont	Belle, West Virginia	120
DuPont	Memphis, Tennessee	120
Rohm and Haas	Bristol, Pennsylvania	-+
Rohm and Haas	Louisville, Kentucky	-+
Rohm and Haas	Knoxville, Tennessee	-+
Rohm and Haas	Deer Park, Texas	550
	Total	870

*As of November 1974.

+All four plants of Rohm and Haas distill methyl methacrylate from crude monomer, which is produced at Deer Park, Texas.